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Applicability of the dual isotopes $\delta^{15}N$ and $\delta^{18}O$ to identify nitrate in groundwater beneath irrigated cropland

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ABSTRACT

Identification of the nitrate sources that adversely impact groundwater quality is a necessary first step in the control of this major worldwide pollutant. The impact of nitrate leachate from urea-ammonium nitrate (UAN) (50% urea-N, 25% ammonium-N, 25% nitrate-N) fertilizer, whose use has increased dramatically in the last three decades largely because it can be applied through sprinkler irrigation systems to corn in all growth stages, is investigated. The dual isotopes $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ were measured in groundwater samples from 39 irrigation wells in two intensively sprinkler-irrigated, corn-growing areas of Nebraska with nitrate-contaminated ($N > 10$ mg/L) groundwater and documented UAN use to ascertain whether nitrified ammonia and nitrate fertilizers can be distinguished in the High Plains aquifer. The areas, which are highly vulnerable to nitrate leaching and differ only in the composition and thickness of their unsaturated zones, are uniquely suited to provide scientific evidence of the feasibility of identifying nitrate fertilizer leachate in groundwater and thereby add significantly to the small body of existing and inconclusive data. The dual isotope method (DIM) results indicate that the nitrate contamination in 38 wells is mostly nitrified ammonium fertilizer. Most importantly, nitrate fertilizer from UAN was not identified isotopically in groundwater beneath almost all fields with documented heavy UAN use. This could be a potentially valuable finding for fertilizer management or it could convey limitations on the appropriateness of the DIM for nitrate fertilizer source identification in groundwater. Slightly enriched $\delta^{15}N_{NO3}$ values in a few wells coincide with the practice of wintering cattle on corn stubble, which reportedly occurred more frequently in one focus area. The absence of natural soil-N leachates and denitrification in groundwater enabled an apparently reliable identification of manure leachates in both areas.

1. Introduction

Leachate from nitrogen (N)-fertilized, irrigated farmland in Kansas, Nebraska, Oklahoma and Texas is the major nonpoint-source of contamination in the underlying High Plains aquifer (Gurdak and Qi, 2006). Since 1980 urea-ammonium nitrate fertilizer (UAN) (50% urea-N, 25% ammonium-N, 25% nitrate-N) has increasingly replaced anhydrous ammonia as irrigated-corn producers' commercial N fertilizer of choice, and by 2005 it was the predominant commercial N fertilizer applied in Nebraska (Ferguson, 2015). The use of potentially explosive ammonium nitrate fertilizer declined precipitously after the 1995 Oklahoma City bombing, and its use is very limited in the central Plains (Stewart, 2008). Potassium nitrate (KNO_3) and calcium nitrate ($Ca(NO_3)_2$) are considerably more expensive and are used infrequently by Midwestern producers. $\delta^{15}N$ values for fertilizers sold in Nebraska range from −2 to +2‰ for urea-N and ammonium-N in UAN and from +3 to +7‰ for nitrate fertilizer (Spalding et al., 1982). Worldwide nitrate fertilizer $\delta^{15}N$ values average + 2.75‰ (Hübner, 1986). Nitrate is the most-enriched commercial N fertilizer formulation reported (Mariotti and Letolle, 1977; Spalding et al., 1982; Hübner, 1986; Fernández et al., 2017). Atmospheric oxygen with a $\delta^{18}O$ of +23.5‰ (Kroopnick and Craig, 1972) is the oxygen source for synthetic nitrate; thus, its oxygens should be similarly enriched. Theoretically, then, the nitrate and ammonium components of UAN, the only nitrate fertilizer

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commonly applied to irrigated corn fields in Nebraska and the Midwest, can be differentiated by their dual isotope (DI) $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ values.

Previous investigations focused on identification of nitrate fertilizer in groundwater using the dual isotope $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ method (DIM) have been inconclusive possibly because the studies were constrained by either inadequate documentation of N fertilizer application rates or areal extent. In one of the earliest investigations enriched $\delta^{18}O_{NO3}$ values of ~ + 13‰ were expected in leachate from ammonium nitrate-fertilized cropland upgradient of a septic plume but were not detected (Aravena et al., 1993). In Germany nitrate fertilizer leached through forest soils was identified by its $\delta^{18}O$ signature; however, the quantity of nitrate leached was dependent upon the amount of soil microbiological activity (Durka et al., 1994). Mattern et al. (2011) identified nitrate fertilizer in only two of 114 samples collected in a partially agricultural region overlying the Brussel Sand Formation in Belgium. Heavy $\delta^{18}O$ values (~+18‰) characteristic of $Ca(NO_3)_2$ fertilizer leachates were reported during winter in a fine-textured soil lysimeter study conducted in Switzerland (Mengis et al., 2001). In summer, however, light $\delta^{18}O$ values in lysimeter experiments suggested that soil microbiological activity during the warm season resulted in rapid immobilization of nitrate in the fine-textured soils with the resulting organic-N subsequently mineralized to ammonium and later nitrified. Mengis et al. (2001) postulated that the immobilization process should be much less pronounced in sandy soil where leaching rates are greater. In Ireland Minet et al. (2012) also found lysimeter soil-water $\delta^{18}O_{NO3}$ values in the range of nitrified ammonium that were of "little use" in identifying nitrate fertilizer in infiltrating N-source mixtures. However, in two spring barley plots with nitrate inputs below crop requirements, $\delta^{18}O_{NO3}$ values approximated those of infiltrating nitrate fertilizer. They cited both Mengis et al. (2001) hypothesis that mineralization–immobilization turnover processes likely cause the low $\delta^{18}O_{NO3}$ values and an alternative hypothesis that crops preferentially take-up nitrate while ammonia remains for nitrification and leaching (Roadcap et al., 2002).

This investigation's primary objective was to determine whether the DIM can successfully identify nitrate fertilizer in nitrate-contaminated ($N > 10$ mg/L) groundwater in two expansive, sprinkler-irrigated, corn production areas of Nebraska that are highly vulnerable to leaching and have well-documented, long-term histories of UAN fertilizer use that are unique to this investigation. Similarly fertilized, sprinkler-irrigated, corn-growing areas are present throughout much of the High Plains in South Dakota and Kansas. A secondary purpose of this DIM groundwater investigation was the identification of minor sources of $\delta^{15}N$ enrichment by eliminating isotopic fractionation effects of denitrification.

2. Materials and methods

2.1. Investigated areas

The two focus areas – one in the Upper Elkhorn Natural Resources District (UENRD) and one in the Tri-Basin Natural Resources District (TBNRD) – are the best areas in Nebraska (Fig. 1) to investigate component leaching of UAN as they are in predominantly irrigated corn-producing areas of eastern and central Nebraska where ~80% of Nebraska's irrigated corn is grown (USDA-NASS). Nebraska is the United States' third largest producer of corn for grain and more hectares are planted to corn than any other row crop. In 2013 ~80% of the 2.8 million corn hectares were irrigated (USDA-NASS). Corn is Nebraska's largest consumer of commercial N fertilizer. The UENRD focus area is underlain by 274,200 contiguous hectares of nitrate-contaminated groundwater north of the Elkhorn River in Holt and Antelope counties while the TBNRD focus area is underlain by 34,820 contiguous hectares of nitrate-contaminated groundwater south of the Platte River in Phelps and Kearney counties (Exner et al., 2014). In the UENRD and TBNRD, 61% and 75%, respectively, of their nitrate-contaminated focus area is cropped; ~85% and 84% of the cropped hectares, respectively, are irrigated; and 54% and 62% of the irrigated hectares, respectively, are cropped to corn. UAN fertilizer use histories are well-documented by the producers. Irrigation water is applied almost exclusively through a center-pivot system designed to evenly apply water to a large area (≥50 ha) of very permeable soils through overhead sprinklers. Many producers apply UAN through the sprinklers, a technique

known as fertigation. Cattle are wintered on the corn stubble of many irrigated corn fields with the practice more prevalent in the TBNRD.

2.1.1. Upper Elkhorn natural resources district focus area

Groundwater nitrate concentrations have been elevated within most of Holt County's contaminated area for four decades (Exner and Spalding, 1979; Exner et al., 2014) and for two decades in Antelope County (Exner et al., 2014) which likely is associated with a shorter period of intense irrigation development. Groundwater in both counties is naturally oxidizing with very low total dissolved solids. Sprinkler irrigation acts as an aerator and return flows likely are further enriched in dissolved oxygen. These soil conditions are not conducive to denitrification.

The 0.2 to 1-m thick soils are mostly well to excessively well-drained, sandy loams with low organic matter (Mahnke et al., 1978; Ragon et al., 1983). Valentine and Thurman, the dominant soil types, have similar characteristics. The top 150 cm are 93 to 97% sand, and soil organic matter (SOM) averages ~1% in the top 10 cm but quickly decreases to ~0.3% at 30 cm (Soil Survey Staff, NRCS). These low organic matter soils are least likely to promote immobilization of nitrate fertilizer. Most SOM likely originates from recently decaying crop stubble and root material. The unsaturated zone thickness beneath irrigated fields generally is > 15 m (Spalding and Hirsh, 2012).

The unsaturated zone is heterogeneous with layers of aeolian sands, sandy silts and silty sands. Continuous clay lenses are absent (Souders and Shaffer, 1969) although isolated clay lenses can occur beneath some irrigated fields. The hydraulic conductivity of the predominantly sandstone aquifer ranges from 6.1 to 45.7 m/day and groundwater flow is predominately to the east except within ~5 km of the Elkhorn River where groundwater flow is toward the river (Pettijohn and Chen, 1982; Peterson et al., 2008). Intense irrigation development of these very permeable soils became possible only with the advent of center-pivot irrigation. Development began in Holt County in the late 1960s and early 1970s and so dominated the landscape that in the 1970s astronauts could identify northeast Nebraska by its lush green circles. Development began in Antelope County in the 1970s and 1980s.

2.1.2. Tri-Basin natural resources district focus area

Groundwater nitrate concentrations in the focus area have been elevated for at least three decades and from 1987 to 2011 concentrations in irrigation wells increased at an annual rate of 0.23 mg N/L to an average concentration of 20.7 mg N/L (Exner et al., 2014). Considered a southern extension of The Sandhills, the area, like the UENRD focus area, is characterized primarily by center-pivot irrigation on highly vulnerable Valentine sandy soils. Depths to water, however, are shallow and average ~6 m (Exner et al., 2014) while the thicker (~58 to 75 m) aquifer is less heterogeneous with relatively thick sand and gravel layers. While most irrigation is by center-pivot, pumping from shallow depths is relatively inexpensive and a few producers continue to furrow irrigate.

In northern Phelps County, groundwater flow is primarily to the east-northeast at ~0.3 m/day and the hydraulic conductivity ranges from 15 to 30 m/day. Farther east in northern Kearney county, groundwater flows parallel to or slightly away from the Platte River and hydraulic conductivities are higher ranging from 30 to 61 m/day (Pettijohn and Chen, 1982; Stanton, 2000). In addition to the shallow depths to groundwater, the higher hydraulic conductivities allow for

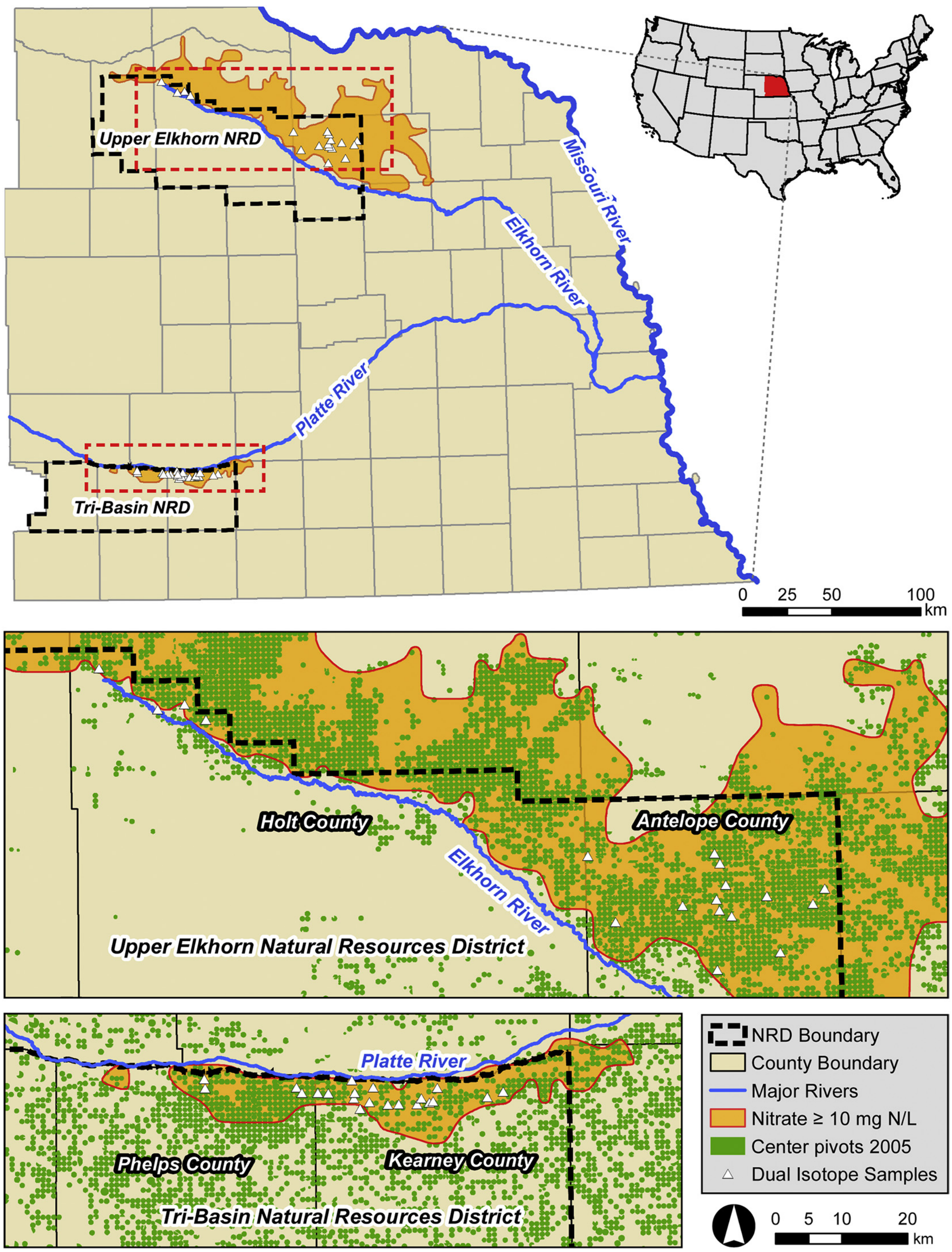

Fig. 1. Dual isotope sampling locations in the Upper Elkhorn and Tri-Basin Natural Resources Districts focus areas in Nebraska.

increased production over shorter distances; thus, wells depths in the TBNRD focus area are considerably shallower than in the UENRD.

2.2. Irrigation well characteristics and sampling

High-capacity irrigation wells usually tap several transmissive zones. Vertically integrated samples from these wells can be excellent indicators of nitrate levels in nonpoint-source contaminated areas (Zlotnik et al., 1995). High nitrate concentrations were shown to occur at all depths in the hundreds of irrigation wells in the UENRD focus area (Exner et al., 2014). Densely-spaced, high-capacity wells likely increase vertical mixing of groundwater (Spalding et al., 2001). Nitrate concentrations in the 39 sampled irrigation wells were not significantly correlated to well depth ($\rho < 0.01$). While many studies have reported higher nitrate concentrations in shallow wells, in this study the closely spaced wells, their large drawdowns and multiple screened depths appear to pull the nitrate downward and homogenize the contamination with depth. All 39 irrigation wells were pumping at least one hour before samples were collected by UENRD and TBNRD personnel midway during the 2013 and 2016 irrigation seasons. Samples for all parameters were collected in 250-ml acid-washed, polyethylene screw-top bottles; immediately placed on ice in coolers until they could be frozen; and later transported on dry ice by University of Nebraska personnel to Lincoln where they were remained frozen until preparation for analysis. NRD personnel documented their observations including manure use and unusual field conditions. Irrigation well data

Table 1
Well attributes, N fertilizer rates, water chemistry and isotopic results for the Upper Elkhorn Natural Resources Districts focus area.

Irrigation Well ID	Irr. Type	Irr. Area	Well Depth	Depth to Water	Pumping Rate	Avg. total N applied	Avg. UAN-N applied	Cl^-	NO_3-N	$\delta^{15}N_{NO3}$	$\delta^{18}O_{NO3}$	$\delta^{18}O_{H2O}$	Calc. $\delta^{18}O_{NO3}$ [§§]
		(ha)	(m)	(m)	(m^3/h)	(kg/ha/yr)	(kg/ha/yr) [§]	(mg/L)	(mg N/L)	(‰)	(‰)	(‰)	(‰)
						2013	2009–13	2013					
190116	CP	40	43	2	284	101	n.a.	< 20	7	4.8	2.4	n.m.	
35236	CP	63	44	12	227	224*	40	< 20	23	2.4	0.9	n.m.	
43348	CP	53	50	15	284	227	49	< 20	27	1.4	1.7	n.m.	
63420	CP	55	59	20	227	177	n.a.	< 20	22	1.7	3.7	n.m.	
77916	CP	55	96	36	204	180	66(4)	< 20	30	2.2	2.5	n.m.	
73220	CP	54	89	29	193	224*	n.a.	< 20	21	3.4	3.1	n.m.	
45204	CP	55	31	12	204	208*	225	< 20	24	2.2	2.7	n.m.	
170957	CP	63	33	13	272	208*	470(4)	20	22	3.5	2.4	n.m.	
33101	CP	65	31	14	227	232	316(2)	< 20	18	3.5	1.8	n.m.	
							2011–15	2016					
70674	CP	73	97	32	182	224*	132	3.0	11	4.2	3.1	−9.7	2.6
46883	CP	88	80	29	227	224*	130	7.4	28	1.9	2.0	−9.3	3.4
70746	CP	41	123	33	141	224*	48	7.7	28	2.8	1.6	−9.6	2.8
47880	CP	53	65	36	193	224*	119	5.2	22	2.0	2.7	−9.8	2.4
170994	CP	53	68	51	193	224*	102(4)	10	26	2.1	7.8	−9.5	3.0
148661	CP	55	85	32	216	224*	90	2.6	11	3.7	2.5	−9.6	2.8
57657	CP	71	53	7	204	224*	0	7.9	8.9	3.2	2.0	−9.6	2.8
81074	CP	58	88	8	238	224*	102(2)	6.7	18	4.6	2.8	−9.4	3.2
83495	CP	52	91	10	204	224*	81(4)	6.3	19	1.5	1.8	−9.0	4.0

[§] 5-yr average unless rate calculated from shorter record as indicated by number of years in parentheses.
[§§] Calculated from nitrification using $\delta^{18}O_{H2O}$ value and $\delta^{18}O_{atm}$ value of +22‰.
* Estimate based on fertilization rate of ~1 lb. N/bu./ac and average 2009–2015 irrigated corn yields of 186 and 200 bu./ac (11.7 and 12.5 Mg/ha, respectively) for Holt and Antelope counties, respectively, (USDA-NASS database) for average fertilization rates of 208 and 224 kg N/ha, respectively; CP: center pivot; n.a.: not available; n.m.: not measured.

Table 2
Well attributes, N fertilizer rates, water chemistry and isotopic results for the Tri-Basin Natural Resources Districts focus area.

Irrigation Well ID	Irr. Type	Irr. Area	Well Depth	Depth to Water	Pumping Rate	Avg. total N applied	Avg. UAN-N applied	Cl^-	NO_3-N	$\delta^{15}N_{NO3}$	$\delta^{18}O_{NO3}$	$\delta^{18}O_{H2O}$	Calc. $\delta^{18}O_{NO3}$ [§§]
		(ha)	(m)	(m)	(m^3/h)	(kg/ha/yr) [§]	(kg/ha/yr) [§]	(mg/L)	(mg N/L)	(‰)	(‰)	(‰)	(‰)
						2009–13	2009–13	2013					
16168	furrow	33	23	2	272	268(4)	n.r.	< 20	18	4.8	3.0	n.m	
100748	CP	57	20	2	204	184(3)	n.a.	< 20	17	3.7	3.0	n.m	
1180	furrow	32	24	2	363	214(4)	n.r.	< 20	11	3.8	2.4	n.m	
24165	CP	61	16	2	238	168(3)	n.a.	21	37	6.9	1.7	n.m	
95264	CP	53	17	5	204	196(2)	227(2)	30	18	5.4	1.9	n.m	
51756	CP	53	16	2	227	151	87	28	53	1.8	2.0	n.m	
21436	CP	65	36	3	182	231	110	28	30	5.9	3.4	n.m	
69144	CP	53	18	3	204	195(4)	154(3)	26	44	0.7	2.3	n.m	
						2011–15	2011–15	2016					
45342	CP	65	28	4	227	302(3)	112(1)	15	28	2.8	2.8	−8.3	5.4
58389	CP	65	33	6	238	254	146(3)	6.2	12	−0.2	2.9	−8.7	4.6
78175	CP	55	29	8	227	239	157(3)	12	17	4.6	2.4	−8.7	4.6
67587	CP	41	23	2	227	237(4)	187(3)	20	7.6	2.1	−1.2	−8.3	5.4
56150	CP	65	32	2	250	131	102(4)	8.6	6.5	3.4	3.1	−9.1	3.8
51869	CP	55	24	2	227	273	206(3)	12	18	2.4	3.4	−8.5	5.0
77529	CP	53	36	3	250	244	128(2)	14	22	2.3	2.3	−8.6	4.8
220269	CP	41	20	2	170	156(4)	156(4)	27	17	7.8	6.8	−8.8	4.4
196895	CP	72	17	2	272	215(3)	236(3)	16	20	2.2	2.8	−8.3	5.4
111984	CP	55	16	2	227	227(4)	210(3)	20	9.3	−0.3	−1.4	−7.9	6.2
39676	CP	55	16	2	227	214(4)	210(2)	23	11	0.8	−0.3	−7.9	6.2
75905	CP	55	27	7	227	152	98(3)	7.7	10	3.3	4.4	−9.3	3.4
77532	CP	53	23	5	227	226(3)	189(3)	9.4	9.5	3.1	2.5	−8.7	4.6

[§] 5-yr average unless rate calculated from shorter record as indicated by number of years in parentheses.
[§§] Calculated from nitrification using $\delta^{18}O_{H2O}$ value and $\delta^{18}O_{atm}$ value of +22‰; CP: center pivot; n.a.: not available; n.m.: not measured; n.r.: not reported as not a reporting requirement for furrow-irrigated fields.

including location, pumping rate, total depth (Tables 1, 2) were obtained from the Nebraska Department of Natural Resources.

2.3. Analytical methods

Samples for nitrate, $\delta^{15}N_{NO3}$, $\delta^{18}O_{NO3}$ and $\delta^{18}O_{H2O}$ measurements were shipped overnight on dry ice to the University of Waterloo's Environmental Isotope Laboratory (EI-lab). Nitrate was measured by ion chromatography with a detection limit of 0.2 mg N/L. The 2013 samples were prepared for $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ isotopic analysis by precipitating NO_3 as $AgNO_3$ (Silva et al., 2000). $\delta^{15}N_{NO3}$ values were measured using an elemental analyzer-isotope ratio mass spectrometer

(EA-IRMS) (Silva et al., 2000) and $\delta^{18}O_{NO3}$ values determined by elemental analysis-pyrolysis (Mengis et al., 2001). The $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ values in the 2016 samples were determined by chemical denitrification to N_2O, pre-concentration, and analysis on a GV isoprime mass spectrometer (Ryabenko et al., 2009). The EI-lab instituted the change in methods as the denitrification method is cheaper and faster and utilizes less sample than the nitrate precipitation method. With both methods $\delta^{15}N$ and $\delta^{18}O$ isotopic precision was ± 0.5‰. $\delta^{18}O_{H2O}$ was measured by isotope ratio laser spectrometry (Kerstel et al., 1999). Isotopic precision was ± 1‰. The stable isotopic N and O compositions, relative to atmospheric nitrogen and V-SMOW, respectively, are represented by $\delta^{15}N$ and $\delta^{18}O$, respectively, and defined as $[(R_{sample}/R_{standard}) - 1] \times 1000$ where R is the ratio of the two stable isotopes ($^{15}N/^{14}N$ or $^{18}O/^{16}O$).

Concentrations of chloride, which can cause interference in the Silva et al. (2000) method, were screened in the 2013 samples using Chemetrics Titrets® titration cell mercuric nitrate method with a range of 20 to 200 mg Cl/L before shipment to the EI-lab. Concentrations in the 2016 samples were measured at the EI-lab by ion chromatography. The detection limit was 0.2 mg/L.

2.4. Fertilizer use

Natural resources district (NRD) personnel reported fertilizer use for each field. Recent UAN application rate data (Tables 1, 2) were obtained from the annual chemigation permit issued by the local NRD and required for each pivot-irrigation system applying chemicals. For decades most producers liberally applied UAN to their irrigated corn fields. UAN also is applied as a side dress and/or broadcast by many producers; therefore, the reported amount of UAN is a minimum. The average annual N fertilizer application rate for the field associated with the sampled irrigation well in the TBNRD focus area and for some wells in the UENRD focus area was obtained from reports the producer must file annually for each irrigated cornfield. For fields in the UENRD focus area that do not have a reporting requirement, an approximate N fertilizer application rate was calculated using the county average irrigated corn yield and the commonly accepted rule of thumb that corn (grain plus residual) removes 1 to 1.2 lbs. N/bu./acre of irrigated corn (Maddux and Halverson, 2008). The estimated rate likely falls short of the actual application rates. The equivalent of 280 to 314 kg N/ha are recommended for yields of 14 to 15 Mg/ha on the low organic matter sandy soils (Shapiro et al., 2009).

3. Results

The DIM sample results are plotted with the $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ envelopes for potential N sources that could impact groundwater within the focus areas (Figs. 2, 3). The $\delta^{15}N_{NO3}$ values of nitrified ammonium fertilizer leachates in groundwater typically range from −4 to +4‰ (Kendall and Aravena, 2000). The envelope overlaps the natural soil-N envelope from +3 to +8‰ (Amberger and Schmidt, 1987). The −10 to +10‰ $\delta^{18}O_{NO3}$ boundary for both potential N sources was determined by Kendall and Aravena (2000) by substituting the lower and upper ranges of soil water and atmospheric $\delta^{18}O$ values in the formula $\delta^{18}O_{NO3} = ⅔\ \delta^{18}O_{H2O} + ⅓\ \delta^{18}O_{atm}$ for nitrification of ammonium in soils (Amberger and Schmidt, 1987). All $\delta^{18}O_{NO3}$ values (Figs. 2, 3) are clearly within the −10 to +10‰ boundaries for nitrification of ammonia. Shallow groundwater $\delta^{18}O_{H2O}$ values should typically reflect the mean-weighted precipitation value (Clark and Fritz, 1997) and are used to approximate the $\delta^{18}O_{NO3}$ formed by soil nitrifiers (Aravena et al., 1993). Average $\delta^{18}O_{H2O}$ values of −9.5‰ and − 8.5‰ in the groundwater of the UENRD and the TBNRD focus areas (Tables 1, 2), respectively, are in the middle of the range for mean-weighted precipitation values reported by Harvey and Welker (2000) for north-central and south-central Nebraska, respectively. Using our average measured $\delta^{18}O_{H2O}$ and $\delta^{18}O_{NO3}$ values in the Amberger and Schmidt

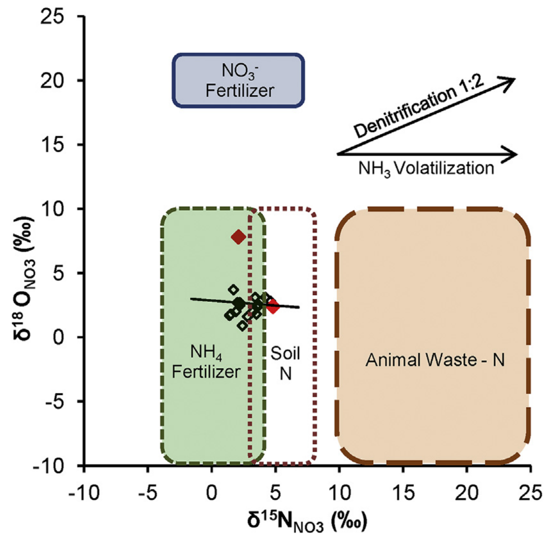

Fig. 2. DIM results for the Upper Elkhorn Natural Resources District focus area. Red symbols identify a sample with an enriched $\delta^{18}O_{NO3}$ value and a sample from a well in a field where manure was observed. Both samples are discussed in the text.

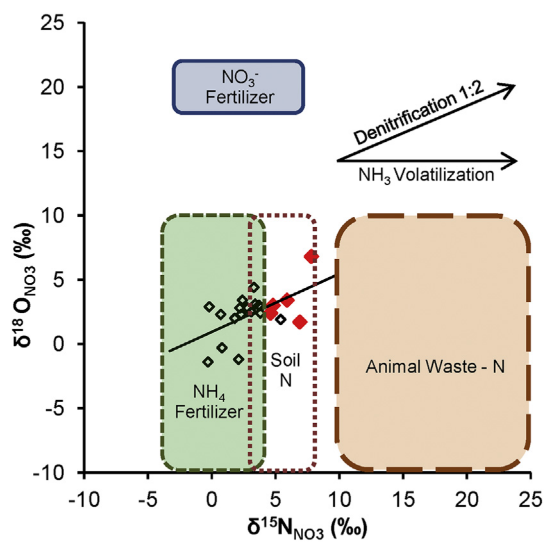

Fig. 3. DIM results for the Tri-Basin Natural Resources District focus area. Red symbols identify wells in fields with observed cattle manure. Both samples are discussed in the text.

(1987) formula, average $\delta^{18}O_{atm}$ values in the UENRD and TBNRD focus areas ranged from +19 to +21‰ and are within the +18 to +22‰ range reported by Amberger and Schmidt (1987). The $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ nitrate fertilizer envelope boundaries are −3 to +7‰ (Spalding et al., 1982) and +18 to +22‰ (Amberger and Schmidt, 1987), respectively.

$\delta^{15}N_{NO3}$ values > +10‰ in groundwater are indicators of animal waste sources (Heaton, 1986; Clark and Fritz, 1997; Mengis et al., 2001; Böhlke et al., 2002; Stanton and Fahlquist, 2006). The +25‰ upper boundary encompasses the +10 to +20‰ range for animal manure first reported by Kreitler and Jones (1975) and most confined animal feeding operation (CAFO) lagoon liquid manure. The $\delta^{15}N_{NH4}$ in 13 Nebraska CAFO lagoons ranged from +2 to +59‰ with only 10% of the values < +10‰ during five sampling events in the same year while the average annual values ranged from +13.7 to +21.8‰ (Mariappan et al., 2009). Liquid hog manure in the San Pedro and Pichidegua agricultural areas of central Chile ranged from +4.1 to +22.2‰

(Fernández et al., 2017). In rural Shijiazhaung, China, heavy $\delta^{15}N_{NO3}$ values confirmed that irrigating with wastewater contaminated groundwater as deep as 100 m (Chen et al., 2006). $\delta^{15}N_{NO3}$ values from > +7 to ~+16‰ suggested that human and animal wastes were major sources of groundwater nitrate contamination in the Jericho area of the Westbank, Palestine (Khayat et al., 2006). Ammonia volatilization is the main mechanism that enriches the light values found in fresh cattle urine (+1.7‰) and manure (+4.8‰) and pig urine (+2.9‰) and manure (+4.0‰) (Gormly and Spalding, 1979) to values ≥ +10‰ in manure and manure slurries. $\delta^{15}N$ values > +13‰ for total reduced N in the compacted manure of feedlots indicate volatilization commences soon after manure deposition (Gormly and Spalding, 1979).

Nitrate-N concentrations in the 18 deep irrigation wells sampled in the UENRD focus area ranged from 7.0 to 30 mg N/L and averaged 20 mg N/L (Table 1). The $\delta^{15}N_{NO3}$ values ranged from +1.4 to +4.8‰ and averaged +2.8‰. The $\delta^{18}O_{NO3}$ values ranged from +0.9 to +7.8‰ and averaged +2.6‰. Except for one $\delta^{18}O_{NO3}$ value in the NH_4 fertilizer envelope, DIM values were in a very narrow range (Fig. 2). Fifteen DIM values were within the nitrified NH_4 fertilizer source envelope. Five of the eight values populating the soil N envelope were in the overlap of the two envelopes. All $\delta^{18}O_{NO3}$ values were considerably lighter than the lower $\delta^{18}O_{NO3}$ boundary (+18‰) for nitrate fertilizer. None of the DIM values populated the nitrate fertilizer or animal waste envelopes. Chloride concentrations in the 2016 samples averaged 6.3 mg/L with a range from 2.6 to 10 mg/L.

Nitrate-N concentrations in the 21 irrigation wells in the TBNRD focus area also averaged 20 mg N/L but had a wider concentration range from 6.5 to 53 mg N/L (Table 2). The $\delta^{15}N_{NO3}$ values ranged from −0.3 to +7.8‰ and averaged +3.2‰ while the $\delta^{18}O_{NO3}$ values ranged from −1.4 to +6.8‰ and averaged +2.4‰. As in the UENRD focus area, 15 DIM values populated the NH_4 fertilizer source envelope (Fig. 3). Five of the 11 values in the soil N envelope were in the overlap of the two source envelopes. $\delta^{18}O_{NO3}$ values < +4.0‰ in 19 of 21 irrigation wells suggest that most of the contamination stems from the nitrification of ammonium from fertilizer and SOM. As in the UENRD focus area, none of the DIM values populated the nitrate fertilizer or animal waste envelopes. Chloride concentrations in the 2016 groundwater samples averaged 15 mg/L with a range from 6.2 to 27 mg/L.

4. Discussion

Nitrate is the most mobile form of N fertilizer and easily moves downward through the soil profile with infiltrating water. Its mobility is markedly faster than that of ammonium or urea, which must undergo microbiological conversion to nitrate. If significantly more nitrate than ammonium fertilizer preferentially leached through the highly vulnerable soils of the focus areas, the $\delta^{18}O_{NO3}$ values would predictably be > +8‰ and potentially approach the nitrate fertilizer envelope. The results (Figs. 2, 3) clearly show that preferential leaching of nitrate fertilizer to groundwater did not occur. Enriched $\delta^{18}O_{NO3}$ values were absent in the groundwater beneath the thin, coarse-textured unsaturated zone of the TBNRD and the much thicker, more heterogeneous, finer-textured unsaturated zone of the UENRD suggesting that fertilizer nitrate is not leached past the crop-rooting zone. The absence of identifiable nitrate fertilizer in groundwater beneath nitrate-fertilized crops supports the early findings of Aravena et al. (1993).

Only one well (170994 in Table 1) in the UENRD had identifiable UAN-nitrate (Fig. 2). The heavier +7.8‰ $\delta^{18}O_{NO3}$ value together with the relatively light +2.1‰ $\delta^{15}N_{NO3}$ value may reflect direct UAN transport either by backflow or by downward movement, possibly from a leaking storage tank, along the unsealed well casing. If UAN directly entered the groundwater, ~25% would be nitrate-N and 75% nitrified ammonium-N and urea-N and the $\delta^{18}O_{NO3}$ fraction would be ~+8‰ if all the ammonium and urea were converted to nitrate in the groundwater and UAN was the only N fertilizer applied.

Further source analysis in the investigated areas is dependent upon the presence of denitrification, which was not expected in the highly oxygenated groundwater and sprinkler irrigation return flows. Enrichment of both isotopes during denitrification is reflected in a positive $\delta^{18}O_{NO3}$: $\delta^{15}N_{NO3}$ slope. An enrichment slope of 0.5 has been confirmed both by theoretical-based computations (Chen and MacQuarrie, 2005; Seiler, 2005) and field studies (Böttcher et al., 1990; Aravena and Robertson, 1998; Mengis et al., 1999; Devito et al., 2000; Fukada et al., 2004; Seiler, 2005; Singleton et al., 2007). The slightly negative slope (−0.18, ρ < 0.01) for the DIM values in the UENRD focus area (Fig. 2) clearly is not characteristic of DI enrichment during denitrification. Thus, fractionation via denitrification appears very limited to non-existent in the thick, heterotrophic unsaturated zone beneath much of the UENRD focus area, and the DIM values should be reliable indicators of N sources.

Fractionation via denitrification would be even less likely in the sandy soils, relatively thin unsaturated zone and highly oxygenated groundwater that characterize the TBNRD focus area. In a DIM investigation at Hastings, Nebraska ~40 km southeast of the TBNRD focus area, denitrification was not evident in oxygenated groundwater samples beneath thick, fine-textured, irrigated soils (Spalding et al., 2018). The slope (m = 0.45) for the DI enrichment in the 21 TBNRD focus area samples (Fig. 3) suggests denitrification. The data (Fig. 4, ρ < 0.01), however, do not show the decrease in nitrate concentration that occurs as the $\delta^{15}N_{NO3}$ enrichment proceeds during denitrification. The conflicting interpretations likely reflect statistical bias introduced in the DI vector from the single enriched sample that is an outlier in both location and surface hydrology. The slope (m = 0.29) of the DI vector without the outlier (well 220269, Table 2) DI values does not support denitrification; thus, the TBNRD focus area isotopic results do not appear compromised by fractionation via denitrification.

Denitrification, known to occur in riparian groundwater immediately adjacent to streams and rivers (Cey et al., 1999; Devito et al., 2000) and in areas contaminated by labile organic matter usually from sewage and animal wastes (Spalding et al., 1993; Aravena and Robertson, 1998), is a possible source of enrichment in well 220269 (Table 2). The well is by far the closest (< 0.4 km) of the 21 wells to the Platte River (Fig. 1) and it is adjacent to a drainage ditch filled with standing water throughout the growing season. Manure from cattle wintered on corn stubble and the well's elevated chloride concentration (27 mg/L) suggest the infiltration of animal waste (Ritter and Churnside, 1990; Karr et al., 2001; Showers et al., 2008). The DIM values ($\delta^{15}N_{NO3}$ = +7.8‰; $\delta^{18}O_{NO3}$ = +6.8‰) could be enriched by

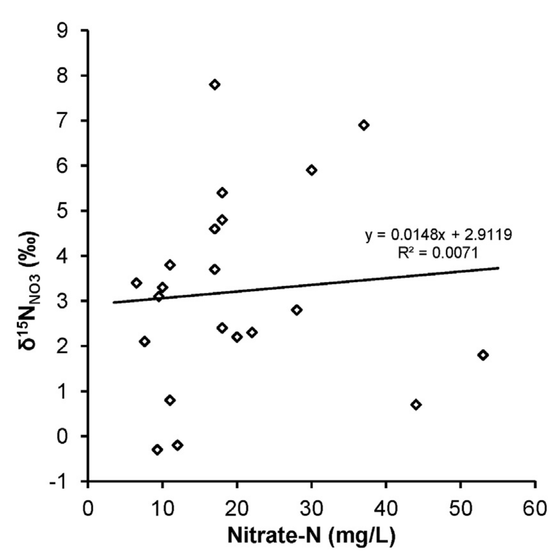

Fig. 4. $\delta^{15}N_{NO3}$ values versus nitrate-N concentrations in groundwater samples in the TBNRD focus area.

several factors or a combination of them. They include capture of Platte River riparian zone groundwater during pumping; infiltration of partially denitrified ditch water; infiltration of manure-nitrate; and infiltration of enriched $\delta^{18}O_{H2O}$ from evaporate in the ditch.

Although soil nitrogen is depicted as a major source of groundwater nitrate in the biplots of both focus areas (Figs. 2, 3), mineralized soil contributions in these areas are considerably less than those from N fertilizer. Most of the labile natural soil-N from these sandy soils (< 1% SOM) probably was released a few years after the virgin sod was broken. Higher organic matter fine-textured soils (silt loams) in central Nebraska north of the Platte River released most of their labile soil N from SOM within the first years of cultivation (Reinhorn and Avnimelech, 1974; Gormly and Spalding, 1979). N fertilization of these soils has increased the aqueous extractable nitrate three-fold and after 60 years of irrigation and cultivation, mineralization of SOM from these silt loams was determined an insignificant source of nitrate in groundwater (Gormly and Spalding, 1979). With considerably less natural SOM and half a century of irrigated corn production in the focus areas, mineralization of SOM residue during the growing season equates to ~22 kg N/% SOM/ha (Maddux and Halverson, 2008) and is much less than the ~225 kg N/ha/yr applied as fertilizer. In a DIM investigation at Hastings, several DI results were in the soil-N envelope. The flat linear increase in $\delta^{15}N_{NO3}$ values into the animal waste envelope together with the N-fertilizer signatures in very shallow borehole groundwater beneath irrigated cropland suggested that soil-derived nitrate leachates did not significantly impact the groundwater (Spalding et al., 2018). The much thinner (< 2 m versus 20 m), coarser and lower organic matter irrigated soils in the TBNRD and UENRD focus areas are not likely contributors of soil-derived N.

Since natural soil N is not a significant N source and denitrification is not blurring the isotopic identity of the sources, the heavier $\delta^{15}N_{NO3}$ values outside the ammonium fertilizer envelope (Figs. 2, 3) likely reflect a mixture of ammonium fertilizer and a heavier N source. Small contributions of nitrified manure leachate with $\delta^{15}N_{NO3}$ values from ~ + 10 to +25‰ could easily explain enrichments of < +2‰. Potential sources of small amounts of manure N include the winter grazing of cattle on crop stubble and, in the TBNRD focus area, the application of manure to some fields. Leachate from nitrified ammonium in manure is a logical suspect in the $\delta^{15}N_{NO3}$-enriched sample (+4.8‰) (Fig. 2) from well 190116 where the producer reported wintering cattle on the field's corn stubble. Manure leachate is suspected in two other wells with slightly enriched (+4.2 and + 4.8‰) $\delta^{15}N_{NO3}$ values in the UENRD focus area. Producers and/or NRD personnel reported animal waste on the fields adjacent to four of the five irrigation wells with slightly enriched (+4.6 to +6.9‰) $\delta^{15}N_{NO3}$ values (Fig. 3) in the TBNRD focus area. Cattle were winter-grazed and manure appears to have been applied to the field adjacent to well 24165 (Table 2). Both the enriched $\delta^{15}N_{NO3}$ value of +6.9‰ and elevated chloride concentration (21 mg/L) can be indicative of animal waste. The same producer used similar practices adjacent to well 78,175 with a $\delta^{15}N_{NO3}$ value of +4.6‰. Cattle also were wintered and manure occasionally spread on the fields adjacent to wells 21,436 and 16,168 which had $\delta^{15}N_{NO3}$ values of +5.9 and + 4.8‰, respectively. Thus, a mixture of ammonium fertilizer and manure-derived nitrate likely is responsible for the slightly enriched $\delta^{15}N_{NO3}$ values within the soil-N envelope (Figs. 2, 3). This is consistent with the results described in Spalding et al. (2018) that clearly showed that both nitrified ammonium leachates from commercial fertilizer and feedlot-associated animal waste applied to irrigated cropland were drawn into the capture zones of several downgradient municipal wells in Hastings, Nebraska.

While manure appears as a minor source of nitrate contamination in both areas, nitrification of ammonium fertilizer is the dominant source of most nitrate in the groundwater of both focus areas. The irrigation practices and N loading; sandy soils and sandy unsaturated zones; and oxic saturated zones in the investigated areas are similar to those found in western Kansas and Oklahoma (McMahon, 2001) and in much of the area underlain by the central High Plains Aquifer (McMahon et al., 2003) where nitrified ammonium fertilizer is the dominant source of groundwater contamination.

5. Conclusions

Our results suggest that the DIM provides a better appreciation of the complexities of the N cycle in the soil rooting zone beneath fields that have received heavy UAN applications for many years. Hypotheses for the absence of isotopically identifiable nitrate in the groundwater are crop removal and/or chemical alteration in the biologically active irrigated root zone. Possibly, timely UAN application results in rapid uptake of the nitrate fraction within the root zone. If correct, this interpretation has major implications for best management practices. More nitrate “spoon feeding” through irrigation systems and less urea and ammonium fertilization could be warranted. The DIM results suggest that application of nitrate using UAN is, for the most part, a beneficial nitrogen management practice. In seasonally warm, bacterially active soil, however, nitrate could be immobilized; reduced to organic-N; mineralized to ammonium; and, in aerobic soils, nitrified (remobilized) back to nitrate (Mengis et al., 2001). In this process, the original atmospheric O_2 would be replaced by soil water and atmospheric O_2 and the oxygen isotope fingerprint in the nitrate would be lost as the oxygen isotopes in the subsequently mineralized nitrate would be isotopically indistinguishable from those in nitrified ammonium fertilizer. Both hypotheses demonstrate that in most agricultural settings application of the DIM to identify nitrate fertilizer in groundwater is questionable. Although sandy soils have low organic matter and high leaching potential, improved water management through sprinkler irrigation systems could increase nitrate fertilizer retention in the root zone and allow uptake and/or immobilization to occur. Studies using isotopically-labeled NO_3 on sandy soils during summer are needed to clarify whether nitrate immobilization and remobilization mask nitrate source identification.

The DIM results indicate that denitrification is not a significant isotope fractionation mechanism in most of the groundwater samples and suggest that reliance on denitrification to reduce nitrate loading to aquifers in irrigated agricultural settings with thick, coarse and/or fine-textured soils could be wishful thinking. The elimination of denitrification and the lack of residual natural soil-N leachates allowed identification of cattle manure as a minor source of $\delta^{15}N_{NO3}$ enrichment in a few samples. The DIM clearly showed that nitrified ammonium fertilizers are the primary source of nitrate in the groundwater beneath both focus areas.

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